Supporting information

Monomolecular VB_2-doped MOFs for photocatalytic oxidation with enhanced stability, recyclability and selectivity

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Experimental Procedures

All chemicals were obtained commercially and used without further purification. Zirconium (IV) chloride (anhydrous, 98%), 2-methylimidazole (98 %) are obtained from Beijing J&K technology Co. LTD. 1,4-benzenedicarboxylic acid (H_2BDC, 98.5 %) is obtained from Tianjin Guangfu fine chemical research institute. 1,3,5-Benzenetricarboxylic acid (H_3BTC, 98 %) is obtained from Zhengzhou Alfa chemical Co., LTD. Vitamin B_2 (VB_2, 98 %) and Titanium(IV) isopropoxide (95 %) are bought from Aladdin. Benzyl alcohol (AR), zinc nitrate hexahydrate (AR) are obtained from Shanghai HUSHI lab. equipment Co., LTD. Bismuth nitrate pentahydrate is bought from Tianjin Kermel chemical reagent Co., LTD. N,N-dimethylformamide (AR), methanol (AR) and n-hexane (AR) are all come from Tianjin Fuyu fine chemical Co., LTDJ.

Synthesis of UiO-66[1]: The synthesis of UiO-66 was according to traditional synthesis with small changes. $ZrCl_4$ (0.212 g, 0.908 mmol) dissolved in 40 mL N,N'-dimethylformamide (DMF) and 1,4-benzenedicarboxylic acid (H_2BDC) (0.136 g, 0.908 mmol) was added. Then another 40 mL N,N'-dimethylformamide was poured into the solution. After stirring at room temperature for twenty minutes, the obtained mixture was sealed and placed in an oven at 120 ℃ for 48 hours. After cooling in air to room temperature the resulting solid was filtered and washed with DMF and methanol repeatedly. Finally, the obtained white powder was dried at 60 ℃.

Synthesis of VB_2@UiO-66: The synthesis of VB_2@UiO-66 is similar to that of UiO-66, except that riboflavin was added in the synthesis process of UiO-66. Specifically, $ZrCl_4$ (0.212 g, 0.908 mmol) and 1,4-benzenedicarboxylic acid (H_2BDC) (0.136 g, 0.908 mmol) were dissolved in 80 mL N,N'-dimethylformamide (DMF) at room temperature. Then different amount of riboflavin (5 mg / 10 mg / 20 mg / 30 mg/ 40 mg) was added in the obtained mixture respectively and the obtained products were named as VB_2@UiO-66-5, VB_2@UiO-66-10, VB_2@UiO-66-20, VB_2@UiO-66-30 and VB_2@UiO-66-40 respectively. The mixture was sealed and placed in an oven at 120 ℃ for 48 hours. After cooling to room temperature in air, the resulting solid was filtered, washed with DMF, deionized water and methanol several times. The color of the obtained yellow powder gradually become deep with the increase of added riboflavin. The obtained powder was dried at 60 ℃ overnight.

Synthesis of Zr@VB_2: Zr@VB_2 were synthesized by the same hydrothermal method as VB_2@UiO-66 by excluding the addition of BDC, in which the molar ratios of Zr/VB_2 are 2:1. $ZrCl_4$ (0.212 g, 0.908 mmol) and VB_2 (0.169 g, 0.454 mmol) were dissolved in 80 mL N,N'-dimethylformamide (DMF) at room temperature. The mixture was sealed and placed in an oven at 120 ℃ for 48 hours. After cooling to room temperature in air, the resulting solid was filtered, washed with DMF and methanol several times.

Synthesis of ZIF-8[2] and VB_2@ZIF-8: $Zn(NO_3)_2 \cdot 6H_2O$ (0.717g, 2.41 mmol) and 2-

methylimidazole (0.180 g, 2.19 mmol) were dissolved in 50 mL DMF. The mixture were sealed in 100 mL Teflon-lined autoclave and placed in an oven at 140 ℃ for 24 h. After cooling down naturally, the obtained ZIF-8 was washed by DMF and methanol to obtain canary yellow powders. The VB_2@ZIF-8 were synthesized following the same steps with 30 mg VB_2 was added into the precursor solution.

Synthesis of MIL-125[3] and VB_2@MIL-125: $Ti(OiPr)_4$ (0.3 mL, 1mmol) and H_2BDC (250 mg, 1.5 mmol) were added in the mixture of 9 mL DMF and 1 mL methanol. The mixture were stirred at normal temperature for 5 min and then transfer into 20 mL autoclave, which was kept at 150 ℃ for 2 d. After cooling down to room temperature, the obtained MIL-125 were washed by DMF and methanol and dried overnight in the fume hood. The VB_2@MIL-125 were synthesized following the same steps with 30 mg VB_2 was added into the precursor solution.

Synthesis of Bi-BTC[4] and VB_2@Bi-BTC: $Bi(NO_3)_3\cdot 5H_2O$ (0.2360 g, 0.49 mmol) and H_3BTC (0.1930 g, 0.92 mmol) were mixed in a mixture of DMF/MeOH (5 mL, 1:3). The solution was then sealed in a 100 mL Teflon-lined autoclave, heated to 120℃ for 45 h, kept at 120℃ for 12 h and then cooled down slowly at the rate of 2℃/min to room temperature. Colorless crystals were washed by DMF, methanol and then dried in air at 60℃. The VB_2@Bi-BTC were synthesized following the same steps with 30 mg VB_2 was added into the precursor solution.

Molecular Oxygen Activation Measurements: In a typical test, 4 mg catalyst was dispersed into 1 mL aqueous solution by ultrasonic process. Then 200 μL catalyst solution was added into 20 mL TMB (3,3',5,5'-Tetramethylbenzidine) solution. TMB solution was prepared using HAc/NaAc buffer solution (pH=4.00) as solvent and the concentration of TMB was 500 μM. The mixture was illuminated by an xenon lamp (300 W) with 420 nm cutoff filter as the light source. The samples were taken at different time intervals for UV-visible spectroscopic measurements. To verify the type of active oxygen species, different scavenger molecules were added into the solution prior to the UV-visible spectroscopic measurements: (1) carotene (20 mg); (2) mannite (50 mM, 1 mL); (3) catalase (4000 unit/mL, 1 mL); (4) superoxide dismutase (SOD, 5000 unit/mL, 1 mL).

Electron Spin Resonance Trapping Measurements: For $^1O_2$: 12 mg samples was dispersed into 3 mL acetone. Then 500 μL suspension of samples was mixed with 5 mL of 2,2,6,6-tetramethylpiperidine (TEMP, 50 mM) solution. For H_2O_2: 4 mg samples was dispersed into 1 mL deionized water. Then 500 μL suspension of samples was mixed with 50 μL of 5,5-diemthyl-1-pyrroline N-oxide (DMPO, 20 mM) aqueous solution. For $O_2^{\cdot-}$: 4 mg samples was dispersed into 1 mL methanol. Then 500 μL suspension of samples was mixed with 50 μL of 5,5-diemthyl-1-pyrroline N-oxide (DMPO, 20 mM) methanol solution. After being illuminated for 4 min, the mixture was characterized using a Bruker EMX plus model spectrometer operating at the X-band frequency (9.4 GHz) at room temperature. An xenon lamp (300 W) with

420 nm cutoff filter was used as the light source.

Alcohol Photo-oxidation Reactions: 20 mg catalysts, 20 μmol of alcohol compounds, and 20 mL n-hexane were placed in a two-neck quartz reactors. The catalytic oxidation reaction was kept at constant temperature (~10 °C) with O_2 bubbling under irradiation with a 300 W Xe lamp (PLS-SXE300, Beijing Perfectlight Technology Co., LTD, China) with 420 nm filter. The yield and type of the product was analyzed by GC-MS chromatography (GC-MS-QP2010, SH-Rtx-Wax column).

Cycle Experiment: The experimental conditions of the cycle experiment is the same as alcohol photo-oxidation reactions. After irradiating for 5 h, the mixture was centrifuged to remove the supernatant and washed several times with n-hexane. Then the powder was employed in the next cycle of reaction after addition of fresh n-hexane solution (20 mL) of benzylalcohol (20 μmol). The irradiation time of every cycle experiment is fixed at 5 hours.

Conversion and Selectivity calculation: The conversion of alcohol and the selectivity of aldehyde in the reaction process could be calculated by the formulas (S1) and (S2), respectively.

$$\mathit{Conversion\ of\ the\ alcohol}\,\% = \frac{C_0 - C_n}{C_0} \times 100\% \qquad \text{(S1)}$$

$$\text{Selectivity}\ \mathit{of\ the\ aldehyde}\,\% = \frac{C_a}{C_0 - C_n} \times 100\% \qquad \text{(S2)}$$

where C_0 is the initial concentration of alcohol before the reaction, C_n and C_a is the concentration of alcohol and aldehyde measured at the time *t*. respectively. The concentration of alcohol/aldehyde were determined according the working curve of peak area vs concentration .

Quantum yield, Turnover number (TON) and Turnover frequency (TOF) calculation: The experimental conditions were similar to alcohol photo-oxidation reactions except that light source was replaced by 450 nm monochromatic light. Number of benzaldehyde molecules was determined by converting GC measurements into moles of benzaldehyde. Incident photons flux was calculated by measuring incident light power with a power meter, taking the photon wavelength equal to 450 nm. Illuminated sample area was π cm^2, and incident light power was 38 $mW \cdot cm^{-2}$, thus giving a typical incident photon flux of 9.1×10^{20} photons h^{-1}.

Quantum yields (Φ) were defined as the number of the product molecules divided by the number of absorbed photons (eq. S1).

$$\Phi = \frac{product\ benzaldehyde\ molecules\ [mol/s]}{number\ of\ incident\ photons\ [einstein/s]} \times 100\% \qquad (S3)$$

In this work, adopted VB_2 are thought as a reactive site:

$$TON = \frac{Total\ moles\ of\ product\ synthesised}{Total\ moles\ of\ active\ sites} \qquad (S4)$$

$$TOF = \frac{TON}{Time}[h^{-1}] \qquad (S5)$$

Characterizations Methods: X-ray diffraction (XRD) characterizations were carried out on a Bruker AXS D8 with Cu Kα radiation (λ = 1.54178 Å). Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) curve were performed on Pyris Diamond spectrometer. Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy was performed on a Bruker ALPHA spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an Thermo ESCALAB 250XI spectrometer. Scanning electron microscope (SEM) photograph was measured by Hitachi S-4800. The UV-Visible diffuse reflectance spectra (DRS) were performed on a Shimadzu UV-2550 recording spectrophotometer, which was equipped with an integrating sphere and $BaSO_4$ was used as a reference. The steady-state fluorescence spectra and phosphorescence spectra were collected on Edinburgh fls1000 fluorescence spectrophotometer.

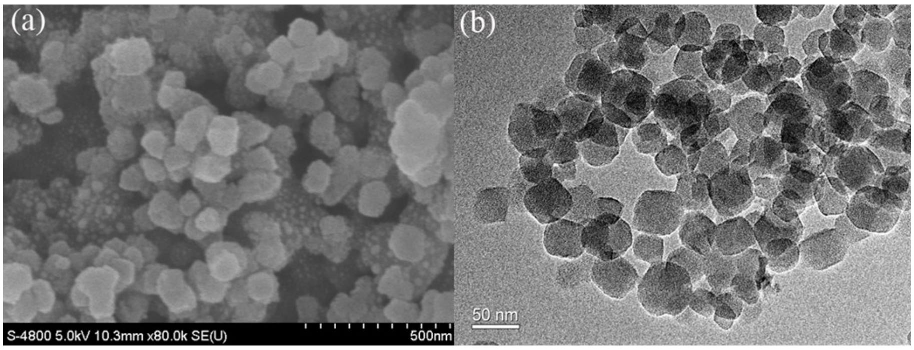

Figure S1. (a) SEM and (b) TEM images of UiO-66. (The small particles in Fig. S1a were gold which were sprayed before the SEM operation to increase the conductivity.)

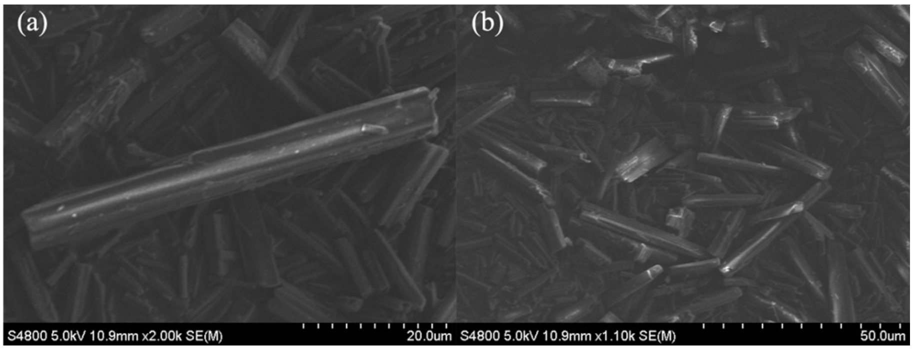

Figure S2. SEM photograph of VB_2.

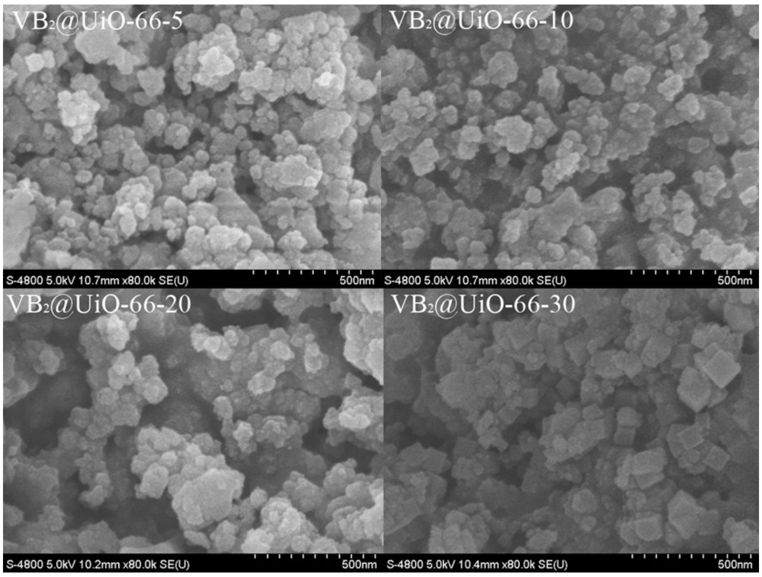

Figure S3. SEM images of VB_2@UiO-66-5, VB_2@UiO-66-10, VB_2@UiO-66-20 and VB_2@UiO-66-30.

Table S1 The BET surface areas and hole radius of different compounds.

Compound	Experimental N_2 BET SA (m^2/g)	Single point average hole radius (nm)
UiO-66	633.5	1.7
VB_2	7.2	6.9
VB_2@UiO-66-5	510.4	2.1
VB_2@UiO-66-10	357.0	2.4
VB_2@UiO-66-20	261.9	2.6
VB_2@UiO-66-30	159.7	2.8

Table S2. Deduced molar ratio of VB_2 to BDC in different compounds.

Compound	VB_2/BDC molar ratio
VB_2@UiO-66-5	0.0069
VB_2@UiO-66-10	0.0104
VB_2@UiO-66-20	0.0123
VB_2@UiO-66-30	0.0142

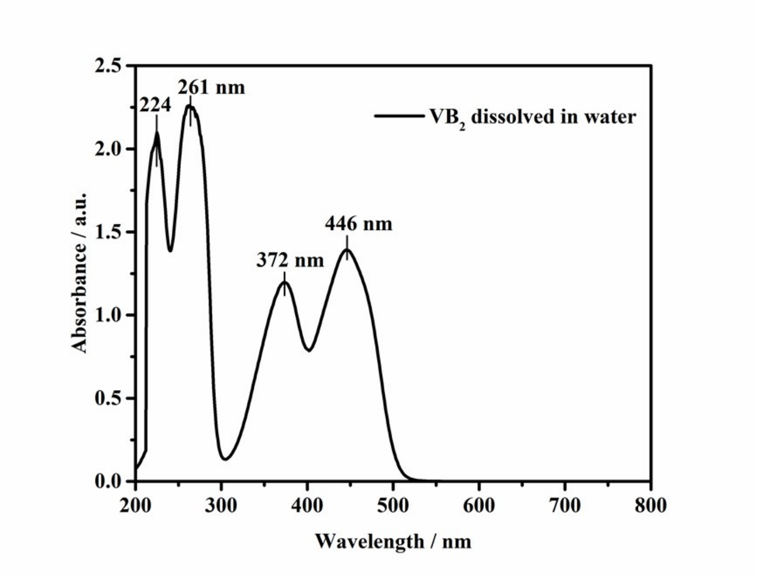

Figure S4. UV-Vis diffuse spectrum of VB_2 dissolved in water.

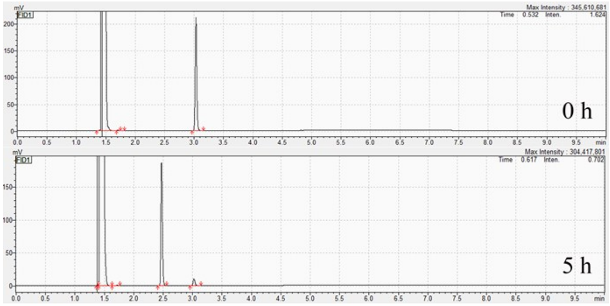

Fig. S5 GC-MS spectra of VB_2@UiO-66-30 after irradiation time of 0 h and 5 h. (And the peaks at 1.42 min, 2.47 min and 3.07 min correspond to n-hexane, benzaldehyde and benzylalcohol, respectively.)

Table S3 Comparison of photo-oxidation ability with different doped MOFs using different complexes.

Photocatalyst	Time /h	Light /nm	Conversion /%	Selectivity /%	TOF /μmol·h^{-1}·mg^{-1}	Ref
MIL-125-NH$_2$-46%	8	> 325	-	-	0.275	5
MR-MIL-125(Ti)	44	420-720	-	100	0.0052	6
QUI-MIL-125(Ti)-16~18%	40	420-780	88	> 99	0.220	7
Ru(bpy)$_3$@MIL-125-NH$_2$	5	>450	-	-	248	8
UiO-66-NH$_2$-F	24	Visible light +80℃	53.9	> 99	24.6	9
UiO-66-NH$_2$-Cl			38.2		17.4	
UiO-66-NH$_2$-Br			43.4		19.8	
Ni-doped NH$_2$-MIL-125(Ti)	10	420-800	21.5	> 99	-	10
M53/GR-8	9	>400	80	100	-	11
FeUiO-66(1:5)	5	>400	32	98	-	12
VB$_2$@UiO-66-30	5	>420	94	100	0.188	This paper

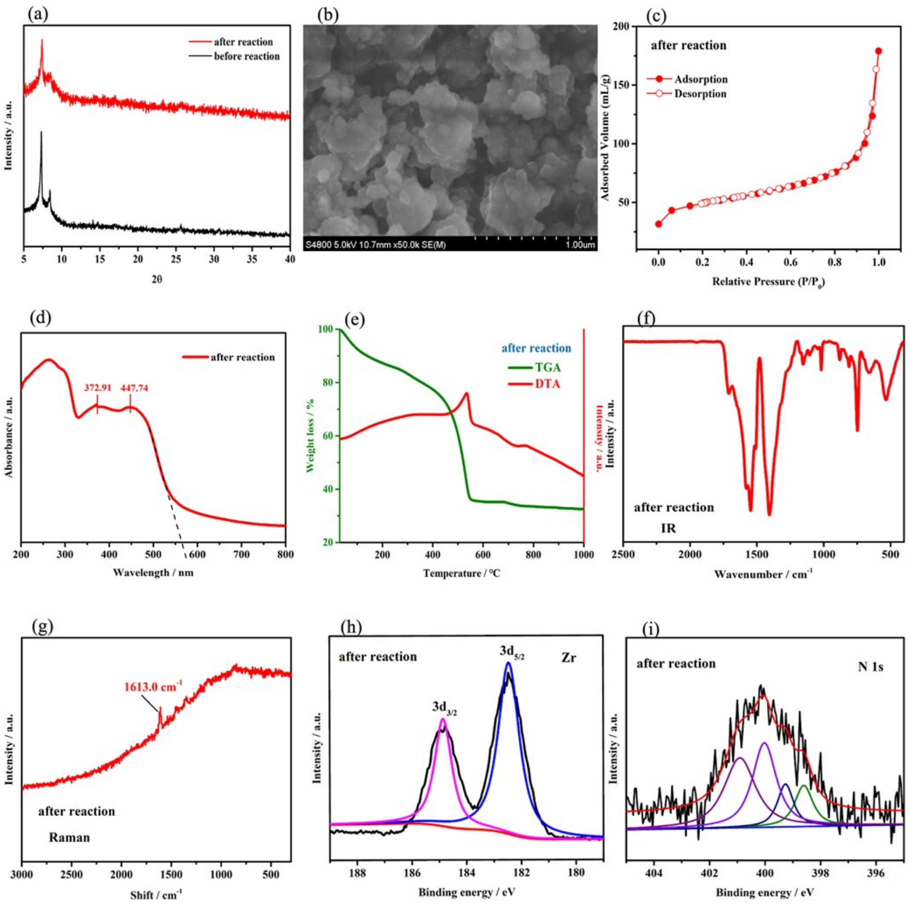

Figure S6. (a) XRD patterns; (b) SEM photograph; (c) Nitrogen adsorption-desorption isotherms; (d) DRS spectra; (e) TGA and DTA curves; (f) IR spectra; (g) Raman spectra; (h) XPS spectra of Zr 3d; (i) XPS spectra of N 1s of VB_2@UiO-66-30 before and after circle reaction.

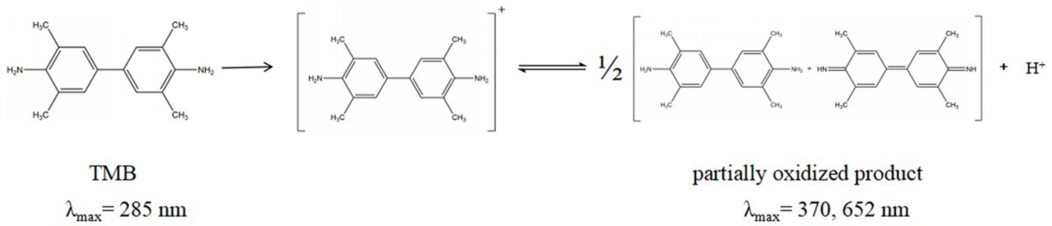

Figure S7. Proposed oxidation pathway of TMB.

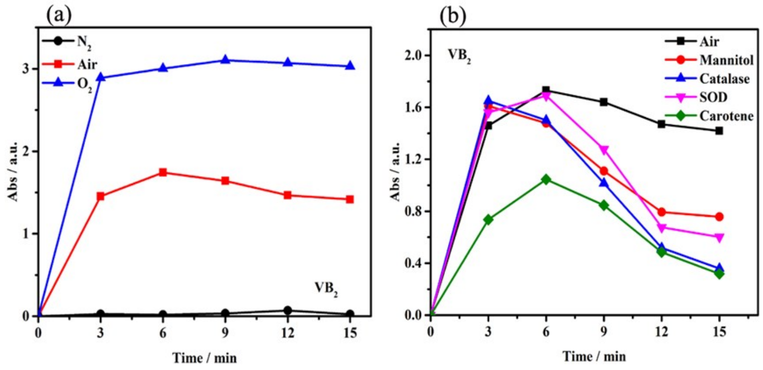

Figure S8. (a) TMB oxidation at 652 nm for VB$_2$ under different gas condition; (b) TMB oxidation at 652 nm for VB$_2$ with different sacrificial agents.

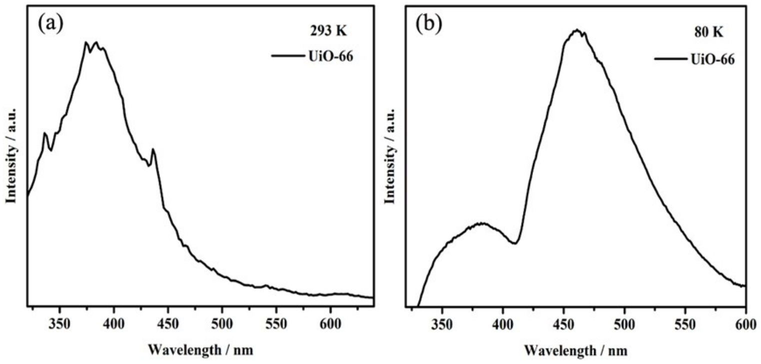

Figure S9. (a) Steady-state fluorescence spectra of UiO-66 at 293 K; (b) Phosphorescence spectra of UiO-66 at 80 K. The excitation wavelength is 300 nm.

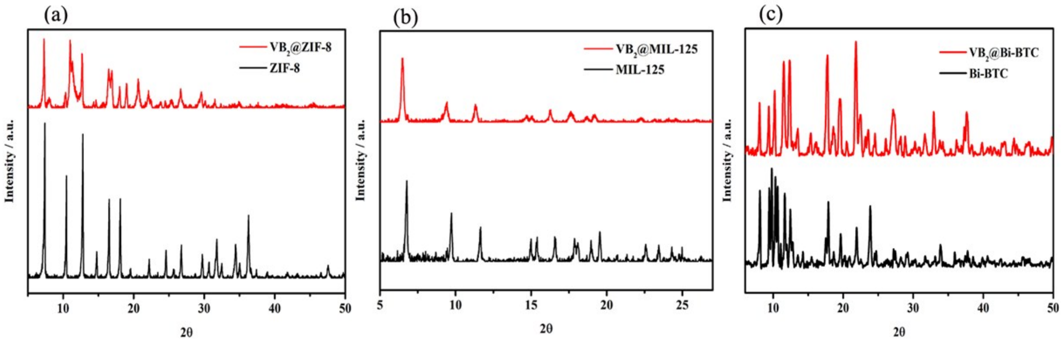

Figure S10. XRD patterns of ZIF-8, VB$_2$@ZIF-8, MIL-125, VB$_2$@MIL-125, Bi-

BTC and VB_2@Bi-BTC.

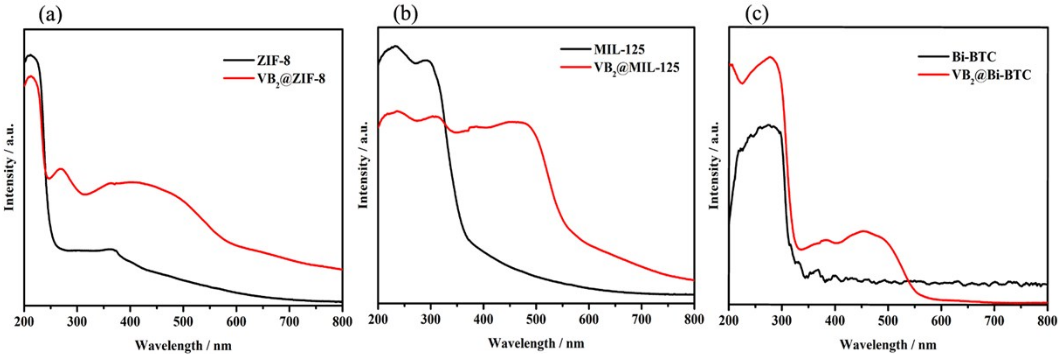

Figure S11. UV-Vis absorbance spectra of ZIF-8, VB_2@ZIF-8, MIL-125, VB_2@MIL-125, Bi-BTC and VB_2@Bi-BTC.

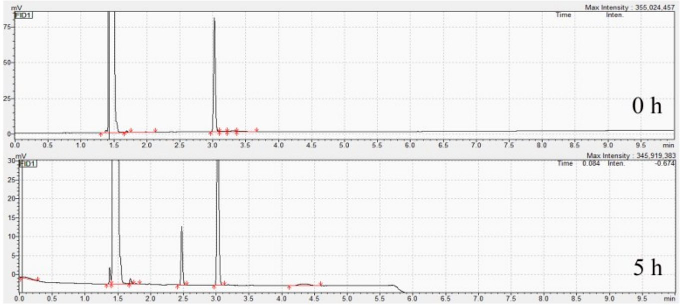

Figure S12. GC-MS spectra of VB_2@MIL-125 after irradiation time of 0 h and 5 h. (The peak at 4.37 min correspond to benzoic acid.)

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